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Up-Scaling of Thermo-Catalytic Reforming Process from Lab to Pilot Scale

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laboratory scale; pilot scale; industrial scale

Abstract

Biomass has become an important approach to meet the current requirements of energy and oil alternatives. In recent years, extensive research has been carried out on the transformation of biological wastes into biofuels and through pyrolysis, which may gradually be replacing the crude-oil resources. One promising pyrolysis route is intermediate pyrolysis. Which opens the field to the valorization of a high variety of biological residues into biofuels including gasses, liquid chemicals and carbonisate. In the present work, the Thermo-Catalytic Reforming-TCR[®] technology based on intermediate pyrolysis with integrated catalytic reforming is discussed, showing high productivity and higher quality biofuels compared to traditional pyrolysis systems. This paper illustrates the data from the up-scaling of the TCR[®] system from laboratory scale to pilot scale using sewage sludge as feedstock. The effects of the design differences are studied from the point of view of the qualities of products, mass and energy balances of the laboratory unit upon the pilot unit.

1 Introduction

Biomass has effective role to meet the present demand of energy and contributes to the achievement of the environmental and energy political targets in terms of climate change. However, parts of the biomass resources are potentially competing with food production, impacting its future competitiveness and negatively effecting political and social acceptance.¹ Therefore, using biological waste as biomass resources is an excellent choice for energy and heat carrier purposes. This approach avoids competition for food production, and achieves bio-products with similar quality like conventional fossil fuels and 1st generation biofuels.²

Compared to other thermal biomass conversion technologies such as gasification, hydrothermal carbonization and torrefaction, pyrolysis provides a better conversion rate of feedstock into a wide range of products, in addition to easily controlled operating parameters.^{3,4} Furthermore, pyrolysis has the advantage that it can be applied worldwide for bio-fuel generation. Pyrolysis converts solid biomass into bio-oil, gaseous, and solid fuels, which can be used as an energy and chemical resources.³⁻⁵

One of the main challenges of pyrolysis is the up-scaling of the systems in scientific principle, in order to enable a wide scale integration of renewable energy sources.^{6,7}

The up-scaling is challenging because of the interdependence of several variables, including the geometry, operating condition and the feedstock properties. The mixing and handling of the solid waste through the reactor is one of the main factors that must be considered during the up-scaling, which is highly constrained by the geometry of the reactor and the physical and chemical properties of the feedstock. Moreover, it is necessary to up-scale the dimensions in order to keep the process parameters approximately the same. Such parameters include residence time, certainly the heat transfer, mechanical energy input, biomass filling in the reactor and biomass conversion rate. Furthermore, gas cleaning, bio-oil condensation and the leakage should be taken into consideration.^{6,8,9}

Pyrolysis of biomass for biofuels production has been studied extensively over the past 25 years and it is still a current topic for research.⁵ The conversion of biological waste into valuable materials through pyrolysis is divided into three types (fast, intermediate, and slow pyrolysis), having different heating rates, reaction temperatures, and residence time, thus showing different yields and product qualities.⁶ The majority of studies focus on fast and slow pyrolysis, and the up-scaling of these systems, hence there are a small number of studies done on the up-scaling technologies of intermediate pyrolysis.

The present research focuses on the feasibility of the conversion of biological residues through the thermo-catalytic reforming (TCR[®]) technology and the up-scaling of the system from laboratory to pilot scale, to achieve an industrial scale unit by understanding and determining the influence of up-scaling on the process.

Previous works have studied the conversion of sewage sludge as a feedstock using fast pyrolysis reactor at wide temperature ranges. The results show that the bio-oil yield is reduced by increasing the reaction temperature above a certain temperature level. Such results are due to the thermal cracking of the bio-oil by secondary reactions, which might enhance the gas yield and gas composition. In terms of the heating value, the fast pyrolysis-oil has a heating value LHV in the range of 17.6–18.4 MJ/kg, it is greatly different from the commercial fuel (LHV > 40 MJ/kg). In view of the fuel properties, it has high water content reaching up to 15–30%, high oxygen content (17–40%), not storage-stable and high viscosity.^{7,10,11}

The results from Deng S. et al.¹², who investigated the effect of increasing the temperature (from 500°C to 900°C) on the products yield through fast pyrolysis, conflict with previous researches. It is shown that the gas yield is reduced from 28% to 15% with higher temperature. Furthermore, the bio-oil yield is increased from 35% to 71%. Conversely, the quality of the gas is increased, represented in the hydrogen percentage changing from 4% to 34% when the temperature is raised from 500°C to 900°C.

Intermediate pyrolysis is studied by Ouadi M. et al.¹³ using deinking sludge. The results show that the bio-oil contained a high heating value of about 36–37 MJ/kg. Moreover, the fuel's physical properties of the produced bio-oil improved when compared to fast pyrolysis bio-oil, as it has a relatively low total acid number (TAN)>5 mgKOH/g and lower viscosity.

The results from Funke A. et al.¹⁴ show that the bio-oil yield is reduced while the gas and carbonisate yields are increased with intermediate pyrolysis processes. This is caused by increasing

the tendency of the secondary cracking reactions. Furthermore, the valuable organic products in the bio-oil - such as benzene and naphthalene - are generated in higher quantity by intermediate pyrolysis.

Pyrolysis bio-oil is not applicable for the direct use in energy conversion because of the poor quality. Hence, an upgrading process for bio-oil is required, which consequently leads to an improvement of the non-condensable gases. The upgrading can be done by filtration, emulsification, solvent addition, catalytic pyrolysis, hydrogenation processing, or steam catalytic reforming.¹⁵⁻¹⁹

A study on microwave catalytic pyrolysis reports a reduction in the bio-oil yield and an increase in the carbonisate yield by using a commercial zeolite (ZSM-5) catalyst. The catalytic cracking reactions are improved and causing an increase of the conversion rate of volatile components to gas. The content of oxygen and nitrogen containing compounds in the bio-oil also decreases significantly in the presence of the catalyst.¹⁷ Other studies have investigated the catalytic pyrolysis of sewage sludge. It shows, that the catalyst enhances the bio-oil heating value and reduces the viscosity.²⁰ Furthermore, it promotes the accumulation of the nitrogen compounds into the char and aqueous phase rather than in the bio-oil. 51.7% of the nitrogen components are converted into solid compounds, thereby increasing the amount of char and about 31.8% of the nitrogen containing compounds are converted into ammonia which is dissolved in the aqueous phase.²¹

Lee Y. et al.¹⁶ studies the upgrading of pyrolysis bio-oil by esterification reaction with methanol, using a tungstated zirconia and amberlyst as catalysts. They conclude that the viscosity of the bio-oil and TAN are decreased significantly by addition of catalysts, and report that an increasing in the calcination temperature from room temperature to 80°C has a positive impact on the bio-oil

upgrading. The results show, that the amberlyst catalyst has more positive impact on the viscosity and TAN reduction.

Another technique used to improve the gaseous fraction and to upgrade the bio-oil is the catalytic reforming, for which the most approved catalysts include nickel or iron based minerals, alkali earth metal minerals, dolomite, olivine and sepiolite. Using the sewage sludge carbonisate as a catalyst also has promising results for the reforming process and enhancing the tar-cracking reactions.^{18,22,23} The results show an improvement in the gas composition through an increase in the hydrogen content. The gas yield is increased, and the condensate yield is reduced. Moreover, there is an increase in the carbon content in the carbonisate due to the reforming process.^{18,19}

In addition, the bio-oil quality is enhanced by the reforming step, when the content of nitrogen and oxygen-containing compounds and the acids in the bio-oil are significantly reduced. On the other hand, the heating value of the bio-oil is decreased, however the HHV of the liquid product is reduced from 16.7 MJ/Kg as pyrolysis liquid to 6.2 MJ/Kg after reforming stage.^{16,19}

The TCR[®] reactor is an intermediate pyrolysis reactor coupled to a post-reformer. For the investigations reported within the paper²⁴, sugarcane bagasse is used as biomass feedstock. The results show a significant enhancement in the products' qualities with the post-reforming and with increasing the post reformer-temperature. The gaseous products without post reforming are in the range of around 6.6vol.% hydrogen and the LHV is in the range of 11.2 MJ/kg, it is raised by the presence of the post-reforming unit up to 28.7vol.% hydrogen with LHV of 14.5 MJ/kg at 700°C. The normal intermediate pyrolysis produces a bio-oil with a HHV of 21.1 MJ/kg, 31.6wt.% oxygen content, 28.8wt.% water content and a TAN number of 12.4 mgKOH/g. When post reforming is applied at 700°C, the bio-oil achieves a HHV of 33.9 MJ/kg, lower oxygen content of 10.2wt.%, 2.6wt.% water content and TAN number of 16 mgKOH/g. Moreover, adding the reforming step and raising the temperature from 500°C to 700°C increases the gas phase yield over the bio-oil

and the carbonisate yield. In conclusion from these results, the reforming stage produces a bio-char with good quality and structural properties, which makes the bio-char suitable as an adsorbent and catalytic support.²⁴

Confirmed by other studies investigating different biological feedstocks like woody biomass, agriculture wastes and digestate for the TCR[®], an increased quality of the products is reported. A notable enhancement in the gas yield and gas quality with increasing reforming temperature has been described. Furthermore, the carbonisate obtains excellent structural and morphological properties (93.1 m²/g BET surface area) suitable for adsorption, catalysis and soil enrichment.^{2,25–}

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The TCR[®] bio-oil shows high HHVs in range of 35–38 MJ/kg according to the feedstock type, with lower oxygen content, between 8.9–3.7wt.%, lower water content between 8.4–0.6wt.%, and TAN number of 5.4–1.8 mgKOH/g. In contrast to fast pyrolysis, where bio-oil with a HHV around 20 MJ/kg on dry base is observed, and high oxygen content is generated.^{10,26,29} Furthermore, the TCR[®] gas has a high hydrogen content up to 40vol.% according to the feedstock type and reforming temperature.^{24,26–28}

The aim of this study is to up-scale the TCR[®] system from laboratory scale to pilot scale, and compare both scales in the point of view of the products distribution and qualities obtained from sewage sludge at different reforming temperatures. In addition, the quality improvement of the products by reforming and the effect of reforming temperature are studied.

2 Materials and Methods

The Thermo-Catalytic Reforming plant TCR[®], as shown in figure 1, is based on an intermediate pyrolysis plant combined with a downstream catalytic reforming unit. The pyrolysis step occurs at moderate temperatures of 400°C–500°C, and a moderate heating rate of 200–300°C/min. The post-

reformer is the stage when the produced carbonisate works as a catalyst at temperatures higher than 500°C. Due to the contact of the pyrolysed gases with the hot carbonisate, the reaction between carbon dioxide and the fixed carbon in the carbonisate is stimulated and enhances the water-gas shifting reactions. The post-reformer operates in a temperature range of 500°C–700°C with the main objective of enhancing the secondary cracking of pyrolysis products, in order to improve the quality of the products.^{2,3,6,26}

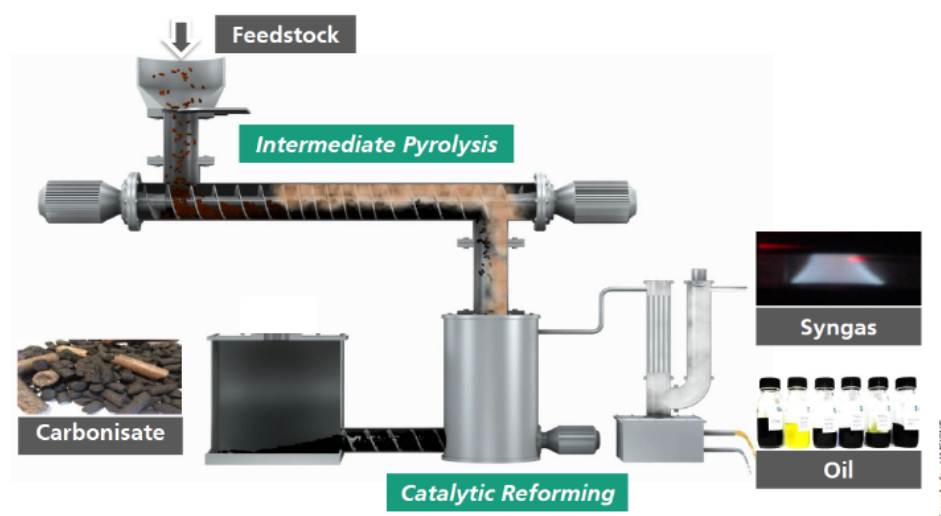


Figure 1. Schematic principle of the TCR[®] process³⁰.

The development of the Thermo-Catalytic Reforming technology at Fraunhofer UMSICHT started with a laboratory-scale (lab scale) (TCR[®]2, 2 kg/h of feedstock input) as a batch process, and was up-scaled to pilot scale (TCR[®]30, 30 kg/h input) for a continuous process. The TCR[®]500, an industrial scale unit, is currently under construction by the ToSynFuel project.^{5,31}

The up-scaling process is divided into several stages, starting with laboratory scale, pilot scale, and then commercial or industrial scale, as shown in figure 2. The up-scaling goes through stages to achieve the final goal of a continuous operational industrial unit. By analyzing the performance of each scale, the capabilities of the technology can be evaluated without taking on the huge

financial risks associated with up-scaling the technology directly from the lab scale to the industrial scale.⁹ Therefore, the design and operation of the industrial TCR[®] plant highly depends on the results from the up-scaling from lab to pilot scale. Thus, it is of great interest to study and demonstrate the quality and yields of the products from each units.

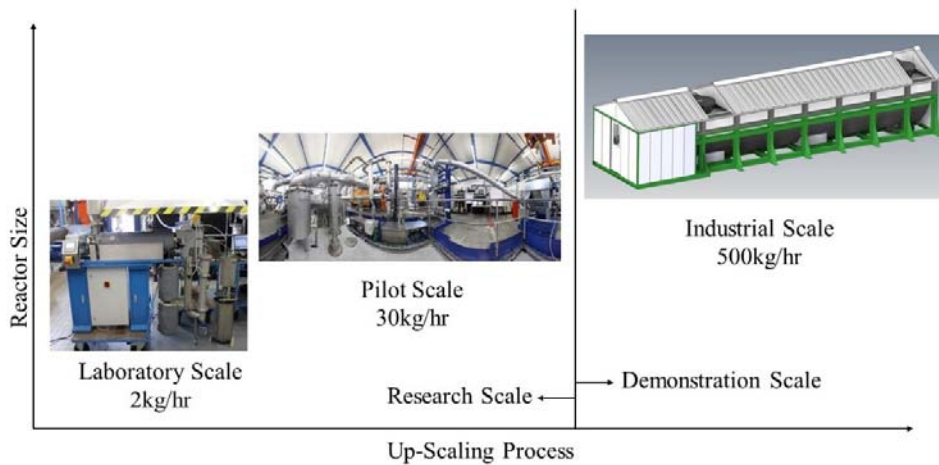


Figure 2. Up-Scaling process diagram

Aramideh S. et al.³² studies the optimum biomass feeding rate through a simulation of biomass fast pyrolysis in a small scale auger reactor using computational fluid dynamics (CFD). When the biomass feed rate is raised from 0.1 kg/h to 2 kg/h, the percentage of biomass particles in direct contact with the heated wall is reduced leading to less biomass being pyrolysed. A similar conclusion is reached by Alexander³³, an up-scaling of the screw geometry by a factor of 10 caused unreacted biomass to leave the reactor, which negatively effects the output products yield.

In large scale, the temperature of biomass reaches the steady state quickly after the first section of the reactor. As validation of these results, a review paper discusses the fast pyrolysis of woody biomass through three scales (0.5 kg/hr, 2 kg/hr, and 25 kg/hr). It shows that up-scaling the system

has a positive impact on the gas yield, and reduces the bio-oil yield, meaning there is an increase in the secondary cracking reactions on the larger scale.³⁴

2.1 Experimental Setup

2.1.1 Thermo-Catalytic Reforming TCR[®]2 Lab Scale

The TCR[®]2 reactor is installed at the site of Fraunhofer UMSICHT, Institute Branch Sulzbach-Rosenberg in Germany. As shown in figure 3, the TCR[®]2 lab scale is a batch system with a feed hopper containing a total biomass capacity of approximately 5 kg. The plant is designed for a maximum mass flow up to 2 kg/h. The feedstock is conveyed through a horizontal pyrolysis reactor with an average residence time of 10 minutes. The reactors are electrically heated with maximum energy input of 16.7 kW/m², it is divided into a three-step screw reactor with different temperature zones. The total length of the reactor is 1000 mm with an inner diameter of 80 mm. Then the pyrolysed biomass is transferred by gravimetry into a vertical post-reformer, with a height of 910 mm and inner diameter of 100 mm. The post-reformer is electrically heated with maximum energy input of 10 kW/m².^{2,24,28}

Within the post-reformer, the vapor residence time is in the range of 4–5 seconds, while the gas remains in contact with the hot carbonisate. The vapors leave the reformer through an upstream vertical pipe and go through two shells and tube coolers at -5°C and 0°C, to ensure complete condensation of the liquid fraction. During each run, it is possible to collect the liquid phase by a gravity settler. Before the outlet, the non-condensable gases go through a washing unit for purification of incondensable gases, then an active carbon filter, candle filter and silica wool filter to eliminate contaminants and particles from the gases. The carbonisate remains in the post-reformer during the testing and it is removed after the experiment.^{2,24,28}

Before the start of each experiment, the system is purged with nitrogen gas for about 15 min, and then the reactor and reformer are preheated up to the required temperatures.



Figure 3. TCR[®] 2 (Lab scale) – maximum capacity 2kg/hr. 1) feed hopper, 2) reactor, 3) post-reformer, 4) gas cooler/ condenser #1, 5) gas cooler/condenser#2

2.1.2 Thermo-Catalytic Reforming TCR[®]30 Pilot Scale

The TCR[®]30 as shown in figure 4, is up-scaled from TCR[®]2 by a factor of 15 with a similar design concept. A summary of technical differences between the lab scale and pilot scale are represented in table S1. TCR[®]30 is a continuous operating unit with a maximum capacity of 30 kg of feedstock per hour. The reactor consists of a feeding unit with a sluice system attached to a three-step horizontal screw reactor with a total length of 2090 mm; inner diameter of 200 mm, and maintaining the solid residence time between 15–18 min. The vertical post-reformer stage is designed with up-scale factor of 15, with dimensions of 1250 mm high and inner diameter 198 mm. The heating unit is divided into four heating zones in the reactor and two zones in the reformer, with a maximum electric energy input of 21 kW/m² and 14.5 kW/m², respectively.

The residence time of the condensable and non-condensable gases in the post-reformer is 4–5 seconds. A high efficiency cyclone is attached after the post-reformer to remove solid particles from the TCR[®]-vapors. To prevent any condensation of bio-oil in the cyclone, the cyclone is electrical heated. The condensation unit is different to that of the lab scale unit, it is a one-step cooler shell and tube heat exchanger, and it is supplied by city waters normally at 8–15°C. In addition, there is an electrostatic participation (ESP) unit installed after the condensation unit. The pilot scale has a cooled continuous carbonisate extraction screw with an separate carbonisate storage container.³⁰ During each experiment, the system is purged with nitrogen gas.

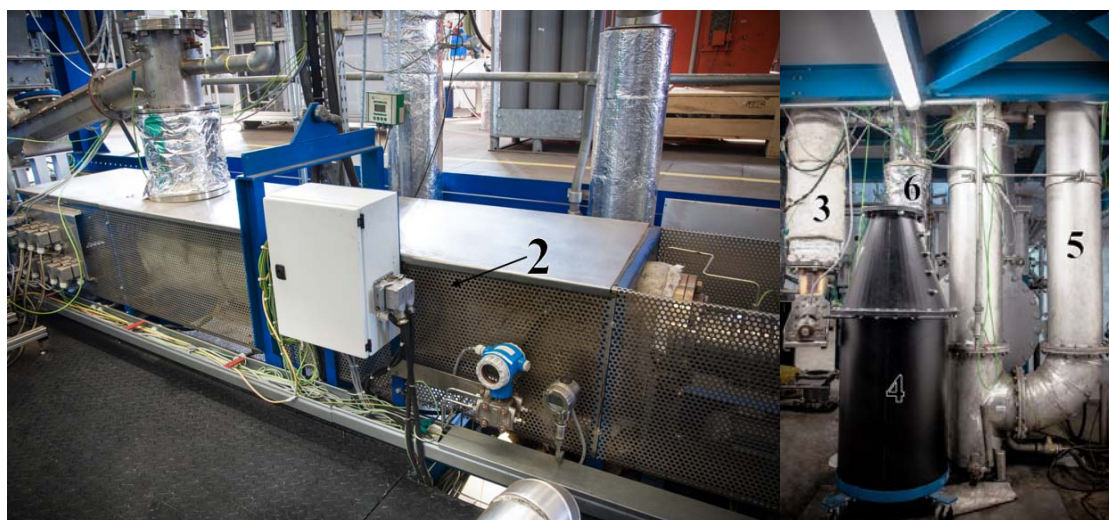


Figure 4. TCR[®] 30 (pilot scale) – maximum capacity 30kg/hr. 1) Sludge system, 2) Reactor, 3) Post-reformer, 4) Solid particle container, 5) Gas cooler/condenser, 6) Cyclone.

The impact of up-scaling on the main pyrolysis parameters - such as heat transfer, heating rate, mixing ratio, solid and gas residence time - are concluded in this paper through several experimental trials in both scales. It is difficult to define the influence of up-scaling on each parameters separately as they are interdependent. Furthermore, the physical, chemical properties

of the feedstock and the operational conditions have an effect on the pyrolysis and reforming process.³⁵

The heat transfer is highly dependent on the mixing efficiency, as well as the screw pitch and rotational speed of the screw. Therefore, the TCR[®]30 has better mixing due to larger screw pitch and longer solid residence time. The pilot scale is expected to have better heat transfer. Due to the large scale, the TCR[®]30 achieves the homogeneous and steady temperature distribution throughout the auger reactor and post-reformer.³⁵⁻³⁷ At the beginning of the reactor, the temperature increasing is slow due to the evaporation of water in the feedstock. Then, the temperature reaches the desired value quickly and stays steady through the second and third sections of the reactor. Hence, this steady state of temperature causes an enhancement in total process.³⁴ More chemical reactions are also expected with the TCR[®]30, such as secondary cracking reactions. Due to the big volume of the post-reformer, the vapors have more contact with the active char.

The variation of the solid biomass and the gas residence time between lab scale and pilot scale is due to the differences in the geometry and mixing ratio of the auger reactors. However, the physical properties of the feedstock are constant through both scales, which has no effects on the residence time.³⁵

2.2 Raw Materials

A municipal wastewater treatment plant in Germany supplied pelletized sewage sludge as shown in figure 5. The ultimate analysis and physical properties of the feedstock are shown in table 1. There is a variation in the chemical composition of sewage sludge samples, because the sewage sludge is a inhomogeneous multi-substance mixture, thus each batch from wastewater dischargers are varying and therefore slightly different in their composition. Additionally the pelletizing and drying processes has an effect on the moisture content.^{11,38} The feedstock is dried and pelletized to have a diameter of 4 mm to 10 mm, length <50 mm, and moisture content in the range of 10–15wt.%.



Figure 5. Feedstock sewage sludge pellets, scale size in cm.

Table 1. Ultimate analysis and physical properties of the tested feedstock sewage sludge

	Unit	TCR [®] 2	TCR [®] 30
C	[wt.%]	30.4	28.8
H	[wt.%]	4.9	4.3
N	[wt.%]	4.3	4.2
O (diff.)	[wt.%]	26.4	18.1
S	[wt.%]	1.3	1.0
HHV	[MJ/kg]	12.4	12.8
LHV	[MJ/kg]	11.0	12.3
Ash	[wt.%]	32.5	37.0
H ₂ O	[wt.%]	12.9	11.3

2.3 Analytical Methods and Measurements

The online gas measurement is carried out by a calibrated pyrolysis gas detector, the system is from Dr. Födisch Umweltmesstechnik AG (MGA 12). The measurement principle is based on an infrared photometer (CO, CO₂, CH₄, and C_xH_y), an electrochemical cell (O₂), and a thermal conductivity detector (H₂). The density and heating value of the gas are measured with an online gas-calorimeter CWD 2005 from Union Instruments GmbH.^{24,28}

The total volume of the non-condensable gasses produced is calculated by difference (Feed-(Σ char+ condensate)).^{28,30}

Elemental analysis (CHNS) is carried out on a dry basis for the both feedstock and the products. The oxygen content is calculated by difference (100-(Σ CHNS+ash)). High heating value was determined by a combustion bomb calorimeter IKA C2000 series from IKA.²⁸

TAN (total acid number) of the bio-oil is determined by 916 Oil Ti-Touch (Metrohm AG). Furthermore, the water content in the bio-oil is measured by Karl Fischer titration using a 915 KF Ti-Touch titrator from Metrohm AG.²⁸

3 Results and Discussion

To demonstrate the up-scale feasibility of the TCR[®] process to industrial scale, the results in terms of quality of the products and mass and energy balance from lab scale (TCR[®]2) and pilot scale (TCR[®]30) are studied. The mean average data are determined from three trials in each system at the same temperature gradients; the experiments are carried out at temperature of 400°C in the auger reactor, and at two different temperature in post-reformer 500°C and 700°C, using sewage sludge as feedstock.

The variety of the qualities and characteristics of the products are due to the process conditions; they are largely independent of the feedstock characteristics. Otherwise, the products yield depends on the initial chemical composition of the feedstock.

3.1 Bio-Oil Characterization

The characteristics of bio-oils from sewage sludge provided by the TCR[®]2 and the TCR[®]30 are represented in tables 2 and 3. In comparison between lab and pilot scales, the bio-oil from the TCR[®]30 has slightly higher quality, represented by lower water content, lower oxygen and lower TAN number. Moreover, the heating value of the bio-oils is almost equal in both units.

TCR[®]2 as a batch system processes only 6kg of feed maximum during single run, and it requires more time to reach the steady state performance, thus less than half of the feedstock is processed during the steady state. This is different to TCR[®]30, while the TCR[®]30 is a continuous process, in which there is enough time to reach the steady state performance, processing therefore more than

90% of the feedstock during steady state. Therefore, the catalytic reforming of the vapors in the TCR[®]30 is higher.

In addition, the good mixing and heat distribution throughout feedstock in the reactor of TCR[®]30 enhances the pyrolysis step and increases the cracking reactions of the bio-oil in the post-reformer. Moreover the larger total residence time of the solid in the TCR[®]30-reactor has an influence in the products.³⁹

A higher content of nitrogen containing compounds is observed in the bio-oil in the case of TCR[®]30 (9.2wt.%), and (7.8wt.%) in TCR[®]2 at 700°C because there are more nitrogen containing compounds in the feedstock that used in the pilot scale experiments, with 4.2wt.% nitrogen while the feedstock used for TCR[®]2 experiments has 4.8wt.% nitrogen. The sulfur content in TCR[®]2 is higher as a result of initial concentration of sulfur components in the feedstock.

Biological wastes usually have higher content of nitrogen and sulfur containing compounds compared to woody biomass or agriculture wastes. For example, bio-oil from wood waste has about 2wt.% nitrogen.^{11,28} However, a previous study at Fraunhofer UMSICHT on the TCR[®] bio-oil showed that it is possible to reduce the nitrogen content significantly by hydro-denitrification (HDN), from 4.6wt.% to <0.1wt.%.²

It is observed that the bio-oil from TCR[®] can be simply separated from the aqueous phase by gravity, due to the strong differences in polarity and density. With gravitational separation, a low water content of the bio-oil can be achieved (<2.7wt.% in the case of a reforming temperature at 700°C, and <3.3wt.% in the case of reforming temperature at 500°C). Compared to the fast pyrolysis of sewage sludge, the bio-oil from the fast pyrolysis cannot be easily separated, as it has a high amount of moisture and it is more acidic.⁷

The 25 most highly concentrated components obtained from Gas Chromatography-Mass Spectrometry (GC–MS) analysis are listed in table S2. Since bio-oil is a complex mixture of

compounds, therefore the small peaks and unidentifiable peaks are neglected. As shown in the table, the main components of the bio-oil from both scales are phenol, benzene and nitrogen containing compounds.^{18,24} The results prove that the bio-oil has a significant low amount of oxygenated compounds and furan derivative due to the catalytic reforming. When comparing the lab and the pilot scale, there is no large tolerance between the components in the bio-oil from both scales.

Raising the temperature from 500°C to 700°C in the post-reforming step has a highly positive influence on the reduction of the oxygen content and the TAN number. In the case of TCR[®]2, the average TAN number reduces from 11.5 to 8.1 mgKOH/g and a low oxygen content averaging 5.8wt.% is achieved at 700°C. In the case of TCR[®]30, the TAN number reduces from 6.8 to 3.8 mgKOH/g, and a low oxygen content averaging 3.2wt.% is achieved. Conversely, the heating value of the TCR[®] bio-oil is slightly reduced by an increased reforming temperature. In the case of biological residues such as sewage sludge, the high reforming temperature increases the cracking of the bio-oil. This is in line with Neumann J. et al.²⁵ for the utilization of digestate from a biogas plant. But this contrasts the results reported by Ahmed E. et al.²⁴. They investigate the conversion of bagasse at different reforming temperatures and observe an increasing in the HHV of the bio-oil by raising the reforming temperature. Nevertheless, in comparison to fast pyrolysis bio-oils, the reduction in the heating value is negligible (< 36 MJ/kg)^{7,10}.

Compared to Yu G. et al.¹⁹ who are using the sewage sludge carbonisate as reforming catalyst, the nitrogen containing compounds in the pure pyrolysis bio-oil at 600°C is 40%, and it is reduced by reforming to 24.8%. Therefore, reforming process at 650°C enhances the oil quality, but it is still lower than TCR[®]-bio-oil. In addition, there is a reduction in the heating value of the bio-oil with reforming process. However, the acidity and viscosity of the bio-oils are also reduced with catalytic reforming.

Moreover, the results from Yu G. et al.¹⁸ show an improvement in the reforming performance by metal catalyst addition. The catalyst increases the decomposition of tar and volatiles during reforming process and shift of the energy content from the bio-oil to the gases, the HHV at 550°C is 34.5 MJ/kg, which is similar to the TCR[®] result.

Table 2. Properties of TCR[®] bio-oil from sewage sludge at 500°C

		TCR [®] 2	TCR [®] 30
C	[wt.%]	75.57	76.46
H	[wt.%]	10.48	9.52
N	[wt.%]	6.75	6.88
O (diff.)	[wt.%]	6.09	4.97
S	[wt.%]	1.11	1.02
HHV	[MJ/kg]	36.24	37.23
LHV	[MJ/kg]	33.90	35.11
H ₂ O	[wt.%]	3.25	2.58
TAN	[mg KOH/g]	11.51	6.80

Table 3. Properties of TCR[®] bio-oil from sewage sludge at 700°C

		TCR [®] 2	TCR [®] 30
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C	[wt.%]	76.67	79.00
H	[wt.%]	8.62	7.85
N	[wt.%]	7.84	9.18
O (diff.)	[wt.%]	5.77	3.17
S	[wt.%]	1.11	0.82
HHV	[MJ/kg]	35.90	37.20
LHV	[MJ/kg]	33.96	35.25
H ₂ O	[wt.%]	2.65	2.08
TAN	[mg KOH/g]	8.06	3.80

3.2 Gas Composition and Characterization

The TCR[®] syngas from sewage sludge contains mainly H₂, followed by CO₂ and CO, as shown in tables 4 and 5. As previously mentioned, the catalytic reforming process in the TCR[®]30 is enhanced by the design of the reactor and the post-reformer, which leads to an increase in the secondary reactions like methane reforming and the water to hydrogen shifting reaction which increases the hydrogen concentration in the gas.

At low reforming temperature (500°C), the results highlight the improvement of the reforming process in the TCR[®]30. The TCR[®]30-syngas has higher hydrogen concentration and lower methane, CO, and CO₂ concentrations. Nevertheless, the higher heating value (HHV) in both scales are similar. At high temperature (700°C), there is more improvement in the reforming step of both scales because of the higher temperature in the post-reformer.

It is expected that TCR[®]2 has a good reforming process because the actual temperature in the post-reformer is higher in the TCR[®]2. Although the heat distribution through the reactor and post-reformer is better in the case of the TCR[®]30. Consistent with Chen J. et al.⁴⁰, the results show more

methane reforming to hydrogen in the small scale, due to the exposure of the biomass to higher temperature. Nevertheless, the gas residence time is equal in both scales of 4–5 sec.

Increasing the temperature from 500°C to 700°C enhances the reforming and catalytic cracking of the pyrolysis products,²³ demonstrated by the high hydrogen concentration. The hydrogen yield is increased from 21.5vol.% to 40.4vol.% in the TCR[®]2, and from 28.7vol.% to 45.0vol.% in the TCR[®]30, indicating higher methane steam reforming reactions in the post-reformer at high temperature.⁴⁰ The HHV also increases with raising the reforming temperatures from an average of 19 MJ/m³ at 500°C to an average of 20 MJ/m³ at 700°C.

In comparison to Yu G. et al.¹⁹, the valuable gas components H₂, CO, and CH₄ are increased with reforming process and with temperature, it is around 14%, 2%, and 5.5% at 500°C respectively, and it is increased to 15%, 6%, and 9% at 650°C respectively. Furthermore, the catalytic reforming with the sewage sludge carbonisate promotes the heating value of the products, while the HHV of gas is increased from 10.2 MJ/m³ to 18 MJ/m³ at 500°C, and from 13 MJ/m³ to 21.2 MJ/m³ at 650°C. Also, it is noticed that the ratio of CH₄/H₂ is decreased by increasing the catalyst ratio, due to the improvement of steam reforming reactions which produces more hydrogen.¹⁸

Table 4. Properties of gas from sewage sludge at 500°C

		TCR [®] 2	TCR [®] 30
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H ₂	[vol.%]	21.47	28.74
CO	[vol.%]	12.67	10.16
CO ₂	[vol.%]	39.93	32.67
CH ₄ *	[vol.%]	6.08	5.46
C _x H _y	[vol.%]	3.42	3.48
Density	[kg/m ³]	1.43	1.06
HHV	[MJ/m ³]	19.03	19.00
LHV	[MJ/m ³]	16.32	16.86

Table 5. Properties of gas from sewage sludge at 700°C

		TCR [®] 2	TCR [®] 30
H ₂	[vol.%]	40.41	45.00
CO	[vol.%]	11.44	9.72
CO ₂	[vol.%]	29.71	21.85
CH ₄ *	[vol.%]	1.1	1.61
C _x H _y	[vol.%]	3.57	2.87
Density	[kg/m ³]	0.95	0.90
HHV	[MJ/m ³]	19.86	21.00
LHV	[MJ/m ³]	17.83	18.82

* The high content of hydrocarbons in the gases influences the detection of the other gases, especially methane caused by a crosswise relation between these compounds

3.3 Carbonisate Characterization

The characteristics of the TCR[®]-carbonisates are presented in table 6. The char formation through both scales remain in pelletized form.

The carbonisates from both scales have high carbon and ash content, and low hydrogen and oxygen content. The higher heating value of the carbonisate did not change significantly with each experiment and averaged 10.3 MJ/kg on a dry basis overall. It is difficult to define the impact of the carbonisate extraction on the products quality, since there are no significant diversities in the carbonisate composition from both scales.

The low H/C ratio is related to steam reforming and tar cracking.¹⁸ Thus, the carbonisates have a high soil stability and could be used for carbon storage in soil.⁶ Due to its high nitrogen content, it can be considered as a fertilizer for plants.¹¹ At the lower reforming temperature, the HHV of the carbonisate from the sewage sludge is found to be around 11–12 MJ/kg. At higher temperatures, the HHV is reduced to 8–9 MJ/kg. The carbonisate can be utilized for heat and power production or gasification. Alternative applications for the carbonisate such as co-firing and gasification for heat and power production, carbon sequestration, tar-cracking catalyst and fertiliser applications also remain promising.^{6,11,23,25}

Table 6. Ultimate analysis and physical properties of the TCR®-carbonisates tested feedstock sewage sludge - from sewage sludge at 500°C

	Unit	TCR®2	TCR®30
C	[wt.%]	28.14	21.33
H	[wt.%]	1.59	1.20
N	[wt.%]	3.29	2.43
S	[wt.%]	1.91	1.44
HHV	[MJ/kg]	10.33	10.06
LHV	[MJ/kg]	7.54	7.34
Ash	[wt.%]	67.90	63.26

3.4 Mass and Energy Balance

The product average yields and distribution from the TCR® systems at different post-reforming temperatures are shown in tables 7 and 8 respectively. The results from the TCR®2 and TCR®30 are very similar, it shows that the up-scaling from lab scale to pilot scale was successful.

The most notable impact on the product yields is the operating temperature and intermediate products residence time through the system. TCR®2 produces higher bio-oil yield and lower gas fraction than TCR®30 at low temperature, because of the steady state period in TCR®30 is longer, which leads to a more steady state of biomass conversion rate, and a better reforming process.

On other hand, at high reforming temperature of 700°C, there is an enhancement in the reforming step in the TCR®2, which produce almost the same yield of the bio-oil and carbonisate as the TCR®30, because the cracking reactions are increased at high temperature. However the gas yield is still higher in case of the TCR®30, and lower yield of condensable gases. These results are in conformity with Brown J. et al.⁴¹ and Idris J. et al.³⁶ In addition, the yield of the aqueous phase

highly depends on the moisture of the feedstock. Although the water content from the different batches of the feedstock is relatively the same, the aqueous phase yield from TCR[®]2 is higher than the TCR[®]30 (28.1wt.% and 20.8wt.%) at 500°C, and (27.9wt.% and 19.3wt.%) at 700°C, respectively.

In accordance to previous studies,^{18,19,24,25} the yield of gaseous fraction is increased, with higher post reforming temperatures, with the opposite effect on the amount of carbonisate and bio-oil. These trends are caused by the catalytic reforming of the products in the post-reformer.

A similar trend is observed by Yu G. et al.¹⁹, in which the catalytic reforming process was carried with sewage sludge carbonisate as a catalyst. The results show that the total condensate (mixture of oil and aqueous phase) yield is reduced from around 20wt.% at 500°C to 10.6wt.% at 650°C by raising the reforming temperature. The lower amount of condensate can be explained by the lower moisture content in the initial feed composition of 6.5%. Matching with TCR[®] trends, the gas yield increases from 24wt.% to 35wt.% at reforming temperatures of 500°C and 650°C, respectively. The carbonisate is slightly reduced by increasing reforming temperature from 500°C to 650°C by 56wt.% to less than 53wt.%. However, the carbonisate yield is higher than the TCR[®] system due to the initial higher ash content (45.6%) in the feedstock.¹⁹

Table 7. Mass balance of products from sewage sludge at 500°C.

Mass Balance	Unit	TCR [®] 2	TCR [®] 30
Carbonisate	[wt.%]	49.4	47.9
Gas	[wt.%]	12.9	24.0
Bio-oil	[wt.%]	9.5	7.3
Aqueous phase	[wt.%]	28.1	20.8

Table 8. Mass balance of products from sewage sludge at 700°C.

Mass Balance	Unit	TCR®2	TCR®30
Carbonisate	[wt.%]	43.1	44.1
Gas	[wt.%]	21.7	29.7
Bio-oil	[wt.%]	7.0	6.9
Aqueous phase	[wt.%]	27.9	19.3

The distribution of carbon in the products is shown in table 9, to understand the influence of up-scaling on the qualities of the products. The carbon balance illustrates the behavior and efficiency of the catalytic reforming process. The results show a slight variation between both scales. There is a deviation in the carbon balances for the gases because the different in the gas yields between the both scales as shown in table 7.

Table 9. Carbon balance of products from sewage sludge at 500°C.

Mass Balance	Unit	TCR®2	TCR®30
Carbonisate	[wt.%]	49.5	44.1
Gas*	[wt.%]	16.6	23.6
Bio-oil	[wt.%]	25.7	23.7
Aqueous phase	[wt.%]	8.2	8.6

*by differences

The energy balance is calculated using the mass balance, water content and the LHV values of each products with respect to the LHV of the feedstock, as shown in tables 10 and 11. Only minor differences between the TCR[®]2 and the TCR[®]30 are noted at both temperatures, therefore the up-scaling the lab scale to pilot scale is successful from the energy content point of view.

The high post-reforming temperatures improves the energy content of the gaseous fraction in favor of the energy content of solid and liquid phase, as observed. There is a slight reduction of the heating energy of carbonisate and bio-oil by increasing the reforming temperature. In general, most of the chemical energy in the feedstock is transferred to the products; moreover, more than 60–70% of the total energy contributed is in carbonisate and gas.

Table 10. Energy balance of products from sewage sludge at 500°C.

Energy Balance	Unit	TCR [®] 2	TCR [®] 30
Carbonisate	[%]	41.4	35.1
Gas	[%]	17.0	26.8
Bio-oil	[%]	34.9	25.0

Table 11. Energy balance of products from sewage sludge at 700°C.

Energy Balance	Unit	TCR [®] 2	TCR [®] 30
Carbonisate	[%]	33.5	36.2
Gas	[%]	45.5	34.5
Bio-oil	[%]	24.3	19.2

4 Conclusion

The up-scaling of the TCR[®] technology from a batch scale laboratory plant to a continuous pilot scale plant was examined through the products' quality, and mass and energy balances. The TCR[®]30 is effective for continuous operation with stable products streams of high quality. It shows that up-scaling has an influence on the heat transfer and residence time of solids and gases through the system, as there is a slightly increase in the pyrolysis and reforming process in the pilot scale. However, the impact of heat transfer and residence time cannot be analyzed independently since such influences are overlapped with other parameters, such as the mixing ratio of the solid biomass, and the exposure time of biomass to the peak temperature in the reactor and post reformer.

The products from both units are found to have higher qualities at a higher post-reformer temperature of 700°C, producing high yield of hydrogen-rich gases. The bio-oils have a very high HHV, they also demonstrate lower corrosive properties and lower oxygen and water content. In general, the results show no big notified differences between the two units, and the up-scaling of the TCR[®] system is a promising to achieve the industrial scale for the production of sustainable energy. Therefore, the next stage is investigating and testing the TCR[®] industrial scale (500 kg per hour continuous feeding).

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Supporting Information

A summary of the technical differences between the TCR[®] laboratory scale and the pilot scale are represented in table S1, it shows the variation in the design and operation conditions. The table S2 presents the Gas Chromatography-Mass Spectrometry (GC–MS) analysis of the bio-oils from both TCR[®] scales, it shows only the highest 25 concentrated components obtained from the analysis, while the small peaks and unidentifiable peaks are neglected.

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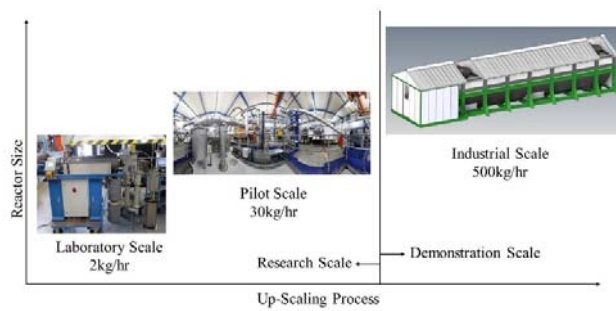
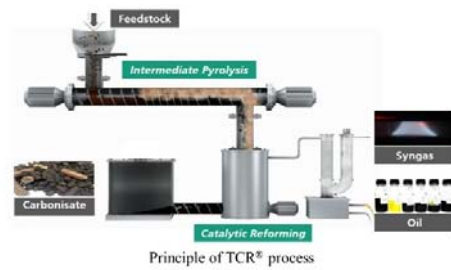
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Table of Contents and Abstract Graphics



Principle of TCR® process